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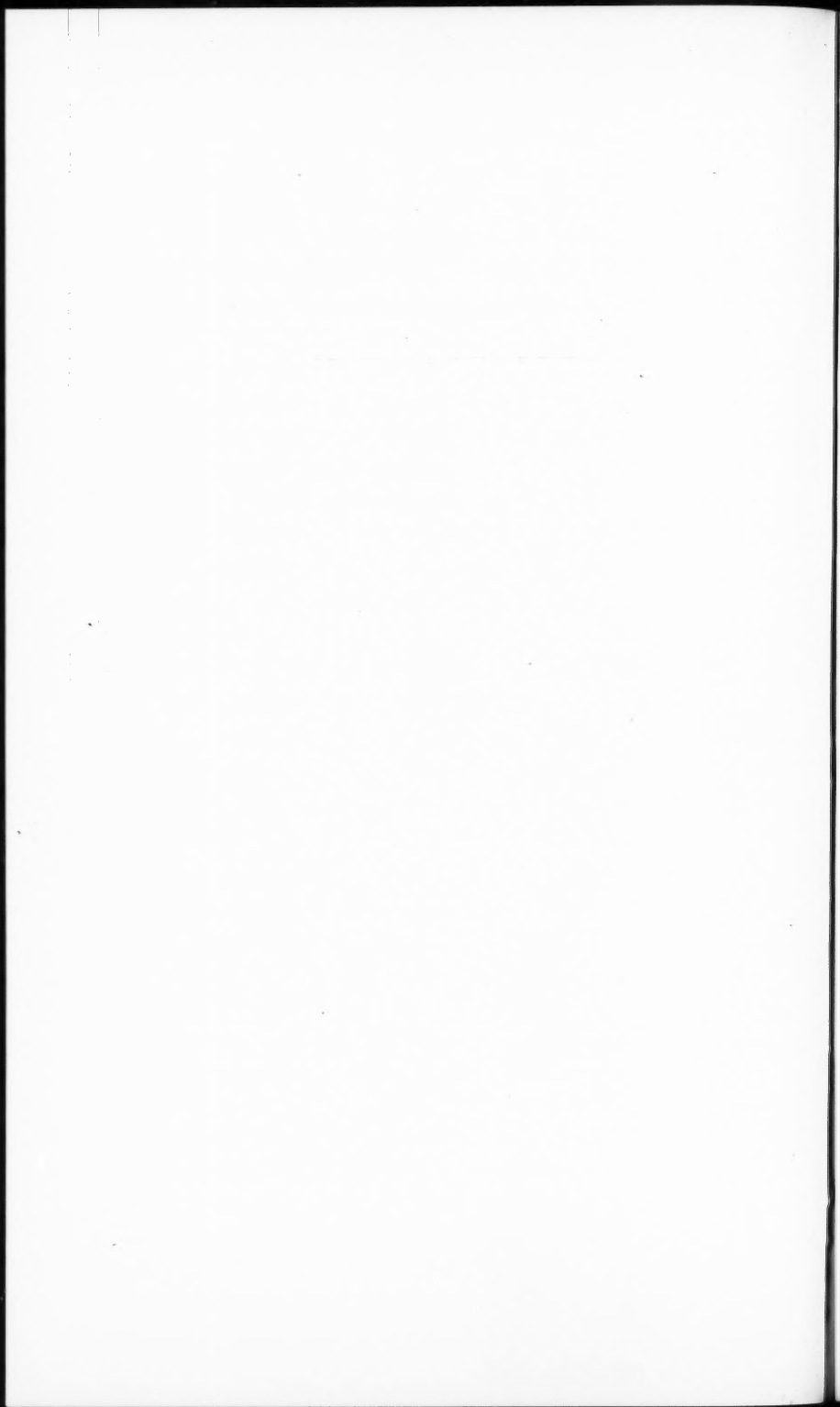
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THE ENTHALPY FOR STEAM FROM 38° TO 125° C

PART V. STEAM RESEARCH PROGRAM

By

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In part IV of the present series of papers on steam properties volumes were recorded to temperatures as low as 195°. The measurements in part were made by the method of confining the steam with mercury; an excellent method provided the upper limit of temperature does not greatly exceed 300°. This restriction is due to the increasing failure with rising temperature of the Dalton rule of partial pressures which must be invoked in correcting for the pressure of mercury in the presence of the confined substances. At temperatures less than 195°, in the case of steam, its strong adsorptive properties probably account for the erratic and irreproducible quality of the results obtained. Earlier and similar experience with other substances led to a belief that the properties of gases at large volumes should be obtained by a method capable of supplying data free from adsorptive disturbances.

There are also other important reasons for developing an experimental procedure especially suitable for obtaining the low pressure properties of gases with high accuracy. Firstly, the statistical theory for low pressure gases is now well advanced and the application of the theory to highly precise data, were it available, could lead directly to exceedingly valuable quantitative information on the properties of the molecular field for pure gases and their mixtures. Secondly, the art of devising empirical analytical forms to correlate the smaller volume data could be based, as it should be, on a really accurate representation of the low (strictly zero) pressure behavior of the gas or gas mixture. In contrast to this the low pressure behavior of the gas is at present obtained of necessity from the correlative equation based on the high pressure data or what is much the same thing, by graphical extrapolation of the high pressure data to zero pressure. Without doubt the present general lack of appreciation of the poor

degree of correspondence of the van der Waals form of equation with the actual behavior of gases could not have persisted had exact low pressure data over a wide range of temperature been available a generation ago.

Work on the method we have attempted to develop was started some years ago (1932)¹ and has been carried through a number of stages, each involving in succession the incorporation in the apparatus of the means of attaining greater precision.

Fundamentally it is aimed to measure $(\delta H/\delta p)_T$, where H is the enthalpy ($H = U + pv$), p the pressure, and T the Kelvin scale temperature, and also C_p the heat capacity for constant pressure. The value of the first quantity for equation of state purposes lies in the fact that it is equivalent to the measure of $v - T(\delta v/\delta T)_p$, or preferably expressed $\left(\frac{\delta v\tau}{\delta\tau}\right)_p$ where τ is the reciprocal absolute temperature. The quantity is zero for an ideal gas and likewise zero for a real gas at a series of pressures and temperatures: the Joule-Thomson inversion points. For a van der Waals molecular model² for example, the quantity is equal to $2a/RT - b$ for sufficiently high temperatures. Here a is proportional to the constant of the molecular attractive force and b to the molecular diameter. It will be clear on consideration therefore that the value of $\left(\frac{\delta v\tau}{\delta\tau}\right)_p$ is a direct measure of the departure of the gas from the ideal state and it may be used generally as a direct statistical measure of the resultant effect of the molecular forces. The thermodynamical equivalent of $\left(\frac{\delta v\tau}{\delta\tau}\right)_p$ is the negative of the product of the Joule-Thomson coefficient and the constant pressure heat capacity, $-\mu C_p$. By measuring μ , or $(dT/dp)_H$ as well as $\left(\frac{\delta v\tau}{\delta\tau}\right)_p$ it is therefore possible to obtain C_p . In practice however it is not possible to measure these differential quantities but only certain

¹ F. G. Keyes and S. C. Collins, *Proc. Nat. Acad. Sci.* 18, 328 (1932). A. Eucken, K. Clusius, and W. Berger, *Zeit. f. Techn. Phys.* 13, 267 (1932) at about the same time published an account of work having for objective the measurement of the same quantity $(\delta H/\delta p)_T$, for air, while we were working with CO_2 , NH_3 and H_2O . The methods, however, were different in detail in accordance with the descriptions given in the cited publications.

² Supposed to possess a positive potential infinite on contact of the molecular spheres of fixed diameter and a spherically symmetrical negative potential with distance index greater than four.

related average values, which through special interpretation may be used to deduce the derivatives.³

In the earlier apparatus the gas was caused to flow at a steady rate through an isolated non-conducting capillary partially stopped with an electrical resistance heater. By adjusting the current in the heater it was possible to annul the cooling effect experienced by the gas through the fall of pressure in the capillary.⁴ Operating however, without current in the capillary resistance heater gave a measure of the Joule-Thomson effect. This in principle is the method employed but the actual practice of the method, especially on low pressure gases, makes it necessary to introduce very complete and carefully controlled radiation screening and heat conduction control. We finally discarded all our earlier results on steam from glass apparatus and turned to the development of an all metal device. During the last year, however, a later all-metal apparatus has been constructed based on the full experience of the past six years for use with other gases and vapors. The results obtained with the first all-metal apparatus seem sufficiently consistent however, to induce belief in their value for extending or at least confirming our knowledge of steam properties at low temperatures.

THE APPARATUS

The design of the apparatus employed is represented in Fig. 1, drawn to scale. The whole equipment was submerged in an oil bath automatically maintained at constant temperature with variations not exceeding 0.001° . Steam entered an interchanger, 1, 2, consisting of a copper tube swaged down upon a twisted copper ribbon. The steam finally entered a low flow-resistance equalizer box, 3, consisting

³ C_p may be defined as $(\delta H/\delta T)_p$

⁴ A. Eucken, K. Clusius, and W. Berger, loc. cit. proceeded differently by allowing the gas to expand through an orifice producing thereby a Joule-Thomson cooling. The gas in its expanded but turbulent state was then returned to its initial temperature, as indicated by the thermocouples, by introducing electrical energy. The ratio of the measured electrical energy to the fall in pressure for a unit of the gas was taken as the measure of the isothermal change of the heat function with pressure. The suggestion that $(\delta H/\delta p)_T$ be measured by using a heater embedded in the plug was made by Edgar Buckingham, Phil. Mag. 6, 519 (1903). We are indebted to Doctor Nathan S. Osborne for calling the reference to our attention. Harvey N. Davis (Phys. Rev. 5, 659, 1915) discussed fully the significance of data for $(\delta H/\delta p)_T$ obtained according to Buckingham's suggestion. This important paper also contains a complete exposition of the various uses of Joule-Thomson data.

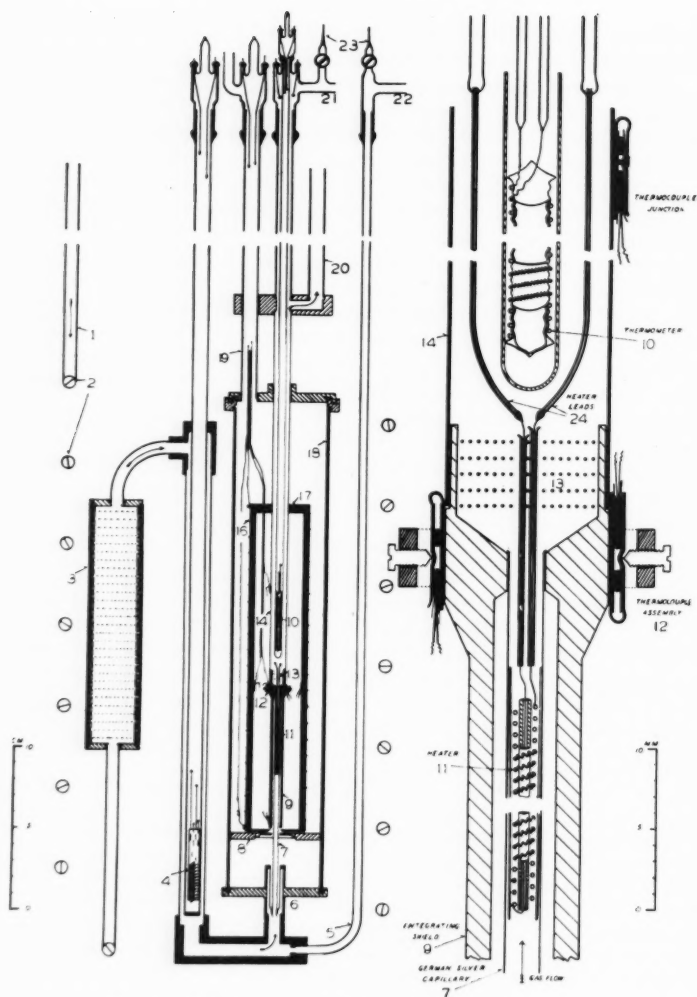


FIG. 1. Calorimeter and Enlarged View of Capillary.

of a large number of gauze disks held in soldered contact with the walls of the container. On entering the calorimeter apparatus the steam temperature was registered on a platinum electrical resistance thermometer 4. The steam then entered the capillary 7, of 2 mm. O.D. German silver having a wall thickness of 0.05 mm. The capillary was joined to a 10 mm. O.D. German silver tube of 0.12 mm. wall, 14, through the intermediary of a massive silver plated copper heat integrating shield, 9, bearing four-junction thermocouples the opposite junctions of which were fastened to the temperature controlled silver plated copper radiation shield 17. The steam passed over the capillary 240-ohm electrical resistance heater, 11, consisting of a No. 40 chromel wire wound in a fine helix and supported upon and within pyrex tubes. The copper plate 8, soldered to the vacuum case 18, prevents heat from being radiated from the heat guard 17 to the capillary 7. It also carries a thin sheet of mica which serves to keep the capillary centered. After passing the 50-mesh copper gauze system 13 designed to equalize the kinetic energy of the steam issuing from the capillary, the temperature is registered by thermometer 10. The steam passes to the condenser by means of tube 20 whilst the pressure on each side of the capillary is obtained through the use of tubes 21 and 22 leading to a mercury manometer.

The tubes 21 and 22 were at substantially room temperature and it was necessary to transmit the pressure of the steam without condensation. This was done by using air in the connecting tubes. During the period when the apparatus was being prepared for use, air was admitted slowly by means of stopcocks 23. The mixture of steam and air was allowed to stream through until the apparatus was about adjusted to begin observations. The cocks 23 were then closed and the air within the system was rapidly swept out leaving an air seal to the manometer which persisted for several hours.

After several attempts to generate steam at a steady rate, a heating element was constructed which floated upon the surface of the water in the generator. The device responded instantly to variations in the energy input: a necessary condition for the satisfactory conduct of the measurements. Manual control of the generator energy input by the operator sufficed to maintain constancy of the pressure drop across the capillary to 0.01 mm. for several hours. The steam admitted to the apparatus was of course superheated.

The effluent steam was condensed in a glass receiver maintained at zero by means of an ice bath. The inside surface of the receiver was treated with oil which produced a condition favoring condensation

and the formation of water drops. The design of the condenser provided for a constant area of surface, an indispensable feature for accurate control of the effluent pressure.

The figure has been prepared to disclose the details of construction of the apparatus but brief comments about several items may be warranted. Thus the thermocouple attachment must provide good thermal contact and at the same time electrical isolation from the shield 9. This compromise was accomplished by hard soldering the thermocouple junction to a copper tab.⁵ The latter was then enclosed in a thin mica film held in a copper clip. There were four of these equally spaced around the shield and pressed thereon by means of steel watch screws supported in a metal collar as shown, 12, in the enlarged drawing at the right of the assembly.

The platinum wire, 0.1 mm. diameter, for the resistance thermometers (28.5 ohms and 23.4 ohms) was machine wound upon a 0.25 mm. steel piano wire in an evenly spaced spiral of 48 turns per cm.⁶ A hollow glass form was then moulded in graphite of the form shown at 10 and used to support the platinum spiral previously released from the steel winding-wire through treatment in hydrochloric acid. The thermometer heads were joined to the metal tubes of the apparatus by means of de Khotinsky cement. The vigorously stirred constant temperature oil bath in which the apparatus was suspended was maintained at a fixed temperature to within better than 0.001° over the period of the observations.

From the construction of the apparatus it will be evident that it is possible to use the apparatus in two ways, and that it may even be used for gases which warm while experiencing a fall of pressure in the capillary (negative Joule-Thomson coefficient). The latter case is important since at temperatures sufficiently above the critical temperature of the gas-liquid phases all gases exhibit the negative Joule-Thomson effect which may be conceived of as due to the preponderating effect of the positive or "repulsive" molecular potential over the negative or "attractive" potential. Thus for a gas composed of the van der Waals model of the molecule, the Joule-Thomson effect is given for low pressures by the expression

$$(dT/dp)_H = \mu_0 = (2a/RT - b)/C_p^\circ$$

⁵ We used essentially the same type of construction employed by Osborne, Stimson, and Fioch, *Bur. Stand. J. Res.* **5**, 425 (1930) in their calorimeter.

⁶ N. S. Osborne, H. F. Stimson, E. F. Fioch, and D. C. Ginnings, *Bur. Stand. J. Res.* **10**, 165 (1933) used this compact coiled type of resistance thermometer. It is believed to have been first described by C. H. Meyers, *Bur. Stand. J. Res.* **9**, 508 (1932).

where the van der Waals a is proportional to the molecular attractive force and b , to the repulsive force manifested on contact of the rigid molecular model spheres (b is four times the volume of the molecules). C_p° is the heat capacity for zero pressure. Helium, for example, at ordinary temperatures is at such a high temperature relative to its critical temperature that the effect of the repulsive potential preponderates and it is now known⁷ that " b " is actually not a constant but a temperature function: a fact substantiated long ago through the viscosity-temperature⁸ behavior of helium. There is enough additional evidence available, similar in kind, to lead to the belief that the behavior characteristic of helium is a general property of all gases although for many, experimental demonstration by known procedures is practically impossible because of the limitations of materials at high temperatures.⁹

MODE OF CONDUCTING THE MEASUREMENTS

The mode of operation of the apparatus used was based largely on the ease with which the results obtained could be interpreted. It is perceived that the quantities to be derived from the measurements, C_p and $(\partial H/\partial p)_T$, are each a function of temperature and pressure. The former quantity may, however, be partially expressed in terms of the latter as follows:

$$C_p = C_p^\circ + \frac{\partial}{\partial T} \int_0^p \left(\frac{\partial H}{\partial p} \right)_T dp \quad (1)$$

It becomes evident therefore that measurements should be made to obtain the energy required to return the expanded fluid to its temperature prior to experiencing the pressure drop Δp . To interpret such data it is convenient to start with a general expression for the enthalpy, H , as follows:

$$H = \int_{T_0}^T C_p^\circ dT + \psi_0 p + \psi_1 p^2 + \dots + h \quad (2)$$

⁷ J. R. Roebuck and H. Osterberg, *Phys. Rev.* **43**, 60 (1933). Joule-Thomson data are given from 83° to 573° K and it is shown that for low pressures the effect is negative throughout the temperature range with a maximum at roughly 423° K.

⁸ Frederick G. Keyes, *Zeit. f. Phys. Chem.*, Cohen Festband, 1927, p. 709; also, *Chem. Rev.* **6**, 175 (1929).

⁹ Steam above 3000° C at low pressure, it is estimated, would exhibit Joule-Thomson properties similar to helium but at these temperatures water could not, of course, preserve its identity nor could apparatus be devised from known materials for measurements.

where the coefficients¹⁰ of the p (pressure) terms are pure temperature functions of the form $\psi_0 = \left(\frac{\partial B_0}{\partial \tau}\right)$, $\psi_i = \left(\frac{\partial \varphi_i}{\partial \tau}\right)$ following from the assumption that for low pressures the pressure of a unit of steam is given by the equation:

$$p = \frac{RT}{v - B} \quad (3)$$

where

$$B = B_0 + \varphi_1 p + \dots$$

It is important for ease of interpretation to have several measurements available at increasing pressure drops for the case of exact temperature restoration. In the more general case we have from (2):

$$H_f - H_i = \int_{T_i}^{T_f} C_p^\circ dT + \psi_{0f} p_f - \psi_{0i} p_i + \psi_{1f} p_f^2 - \psi_{1i} p_i^2 + \dots \quad (4)$$

where subscripts i and f refer to the initial and final states of the gas.

The above equation for restored temperature experiments, $T_f = T_i$, becomes however:

$$[H_f - H_i = -\psi_0(p_i - p_f) - \psi_1(p_i^2 - p_f^2) \dots]_{T_f = T_i} \quad (5)$$

and when data are accumulated at a series of fixed temperatures, ψ_0 , ψ_1 , etc. become known in relation to temperature. With this information it becomes possible to deduce the quantity $\int_{T_i}^{T_f} C_p^\circ dT$

from measurements in which greater amounts of energy, Equation 4, were introduced than required for temperature restoration, ($T_f > T_i$). In the case of steam the measurements were all conducted at initial pressures below an atmosphere where coefficients other than ψ_0 and ψ_1 were not required. The Table I gives a summary of the measurements taken with the apparatus of figure 1.

The saturation pressure at 38.94° C is less than 55 mm. and at 60° C, 149.38 mm. The difficulty of making accurate measurements at these low pressures is considerable in view of the necessity of maintaining a large enough drop to secure accuracy in the measurement of the energy. The rates of flow also become large because of the larger volumes with attendant kinetic effects. The number of measurements at the two lower temperatures were on this account less than at the higher temperatures where the larger available pressure range made possible more favorable conditions for the measurements.

¹⁰ F. G. Keyes, L. B. Smith, and H. T. Gerry, Proc. Am. Acad. Arts and Sci., 70, 341 (1936)

When the details of the measurements became available it was found that a correction of the order of one percent was required in all the measurements. The circumstances making correction necessary are as follows. The figure 1 shows that the copper integrating shield 9 telescopes into the German silver tube 14 to the extent of about 6 mm., the end being located 8 mm. above the capillary exit. The effluent steam had a linear velocity varying from 1000 to 5000 cm. per second. The temperature of shield 9 assumed the temperature of the outgoing steam as indicated by thermometer 10 during the measurements of $(\Delta H/\Delta p)_T$ and also the temperature of thermometer 10 in the measurements for ascertaining C_p° . Taking the former type of measurements for detailed consideration it will be clear that in the circumstances the heater 11 will supply the heat required to compen-

sate for the Joule-Thomson cooling, $\int_{p_i}^{p_f} (\partial H/\partial p)_T dp$, and also a

part of the heat corresponding to the mean kinetic energy acquired by the gas in the course of its turbulent passage through the capillary. Immediately after issuing from the capillary the kinetic energy begins to be dissipated with attendant rise in temperature. Had the telescoping portion of shield 9 and the gauze baffle in contact therewith been long enough, the heat corresponding to the acquired kinetic energy of motion of the steam would have been given to the shield. Since a steady state of flow is maintained, a condition would have ultimately resulted, assuming perfect thermal contact of the heater and thermometer leads with the heat guard 17, whereby exact heat compensation would have been attained and the heat supplied by the heater would have been only that corresponding to the quantity

$$\int_{p_i}^{p_f} (\partial H/\partial p)_T dp.$$

A second factor was the imperfect thermal contact of the heater and thermometer leads with the heat guard 17. The effect of the rise in temperature of the effluent steam at the baffle was therefore to cause loss of heat along the heater and thermometer leads. It is evident that the imperfect thermal contact was more serious in its effect in the measurements where the temperature as indicated by thermometer 10 was considerably greater than the temperature of the bath or as given by thermometer 4.

In order to come to a clearer understanding of the effects referred to, measurements of the temperature effects manifested by a gas after changing linear velocity were carried out with air, carbon dioxide,

ammonia, and hydrogen. The gases were caused to flow in an insulated 10 mm. glass tube having a short section of 2 mm. tube. The temperature effect, δt (corrected of course for the Joule-Thomson effect) proved to be directly proportional to the pressure drop per unit length of the pressure restraining tube or $\delta t \sim \frac{\Delta p}{\Delta l}$ and independent, as would be expected, of the nature of the gas.¹¹ In addition, one junction of a thermocouple was fixed to tube 14 above thermometer 10

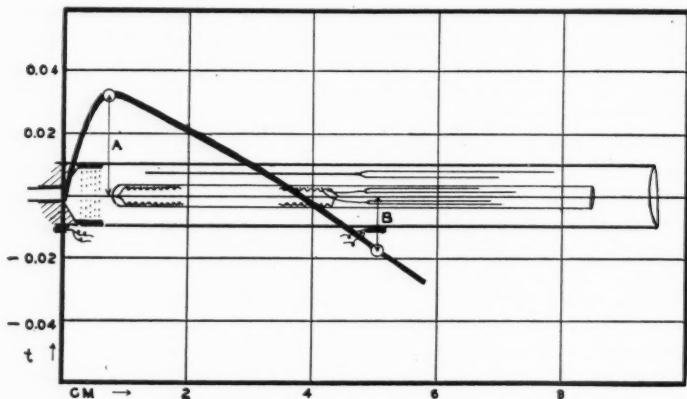


FIG. 2. Variation of Temperature with Distance along Tube 14.

and the other junction to the shield 9 for the purpose of observing similar kinetic temperature effects in steam. At high rates of flow the thermal leakage along the leads was small enough to give a reasonably good measure of the kinetic effects.

Figure 2 is a representation of the temperature along tube 14 from the exit of the capillary past the thermometer 10. The magnitude of δt deduced from the separate flow measurements is given by the empirical relation $\delta t = 0.055 \left(\frac{V}{66} \right)^2$ where V is the volume of steam leaving the capillary per minute. The values of δt in the diagram correspond to the fifth entry at 100° given in table I. The value of

¹¹ An interesting account of a wide variety of experiments on the temperature effects for moving gases is given by J. P. Joule in the second volume of the Collected Works, beginning on p. 215.

δt at B is that measured by a thermocouple junction whose other junction is on shield 9. The temperature at B relative to the capillary end may be either positive or negative in sign for any specific measurement, depending on the conditions of flow velocity and heat input by the heater 11. The resistance thermometer actually measures a mean temperature over its length, but from the relative positions of the thermometer 10 and the thermocouple at B it was deduced that the temperature correction to be applied to the resistance thermometer was 2/5ths of the difference between the temperature at A and at B . The whole correction was of the order of 0.002° for low rates of flow and 0.05° for the highest.

DISCUSSION OF THE RESULTS

The first stage in treating the corrected data given in Table I was to evaluate ψ_0 and ψ_1 as defined by equation (5). It will be noted that at temperatures 38.94 and 59.44 only one constant temperature value of $\left(\frac{\Delta H}{\Delta p}\right)_T$ is available and it is accordingly not possible to determine empirically the quantity as a linear function of pressure. At 80.02, 100, and 125° C, however, the pressure range from the saturation condition to the lowest operable pressures was sufficient to give the pressure dependence of ψ with pressure.¹² It will be observed, however, that in no case is the final temperature exactly equal to the initial temperature. The worst case is measurement 6 at 100° where $T_f - T_i$ is 0.0763. In this as in every other instance the values of C_p° by A. R. Gordon¹³ as corrected by E. Bright Wilson, Jr.¹⁴ were used to compute the "correction" required to reduce the actual experimental values to the values that would have resulted had T_f been exactly equal to T_i . In the worst case, the sixth measurement at 100° , the value of $C_p^\circ \times 0.0763$ amounted to one in forty of $(H_f - H_i)$.

From the data of the $(\Delta H/\Delta p)_T$ measurements at 80.02, 100 and 125° , values were deduced for ψ_0 and ψ_1 . The similar data for 38.94 and 59.44° C were reduced by using ψ_1 values computed from the equation of state for steam. The values are listed in Table II.

¹² It is inferred that the assumption of linear dependance of $(\delta H/\delta p)_T$ on pressure is sufficiently exact within the limits of precision of the present measurements on the basis of the higher temperature volume data (No. IV of the present series of papers).

¹³ A. R. Gordon, J. Chem. Phys. 2, 65 (1934).

¹⁴ E. Bright Wilson, Jr., J. Chem. Phys. 4, 526 (1936). The amount per mol of steam to be added to Gordon's values is $4.08^{-5} RT$, or about a part in 350 for the mean temperature of the experimental range of the present paper.

The values of ψ_0 were smoothed by least square solution of the data for the differences between the observed and equation of state ψ_0 values. It will be noted that $\Delta\psi_0$ becomes negligibly small at high temperatures. Thus at 200° $\Delta\psi$ is 0.0432 I. j. while at 300° it is 0.0043 I. j.

The quantity $\Delta\psi_0$ may be integrated on the assumption that ΔB_0 of the equation of state is zero for $\tau = 0$. Thus we find:

$$B_0 \text{ obs.} - B_0 \text{ cal.} = 0.419 \tau^{12} 10^{30} - 0.0550 \tau^{24} \cdot 10^{60} \quad (6)$$

This leads to a value of $B_0 \text{ obs.}$ 4.1 cc./g. greater than the corresponding B_0 used in the equation of state at 38.94°. ¹⁵ The error this would cause in computing the saturation volumes would, however, amount to only one in six thousand. It does not appear that the volumes of steam below 200° would be seriously modified by the introduction of the new B_0 information provided a part in several thousand is an error of small consequence.

It will be observed from Table II that the ψ_1 's deduced at the three highest temperatures are of the same order of magnitude as those given by the equation of state. The precision with which ψ_1 can be determined depends, however, upon the range of variation of the pressure drop across the capillary heater which is necessarily very restricted at 125° and lower. It is our opinion that the values of ψ_1 "observed" may be in error by twenty percent in the 80 to 125° range and probably by a greater amount at the two lower temperatures. For many calculations at low pressures only the B_0 values are required.

THE C_p° VALUES

The reduction of the remaining data where t_f exceeded t_i was next carried out using the observed ψ_0 and ψ_1 values. The latter quantities correspond of course to the temperatures of the gas entering the calorimeter in the $t_i = t_f$ experiments. The reduction of the heat capacity data requires in addition, however, values of the ψ coefficients for the higher temperature given by thermometer 10. The expressions given at the bottom of Table I were used to compute the desired values of ψ_1 and $\Delta\psi_0$ was used to obtain the "smoothed" difference ($\psi_{0f} - \psi_{0i}$). This difference was then applied to the observed or unsmoothed value of ψ_{i0} to obtain $\psi_{f0} \text{ obs.}$ used in the computations of

¹⁵ The formulation of the equation of state as given in paper No. IV was guided in the neighborhood of 60 to 100° by a knowledge of preliminary ψ_0 values obtained from an investigation using glass apparatus which preceded the use of the present improved all-metal construction of Fig. 1.

C_p° . For temperatures 38.94 and 59.44 the ψ_1 data from the equation of state were used. The part played by the ψ_1 terms at these latter temperatures was of the order of 2 percent. Table II gives the values obtained for C_p° .

The values of C_p° in Table II have been entered in the diagram Figure 3, along with a full line representing the Gordon-Wilson¹⁶

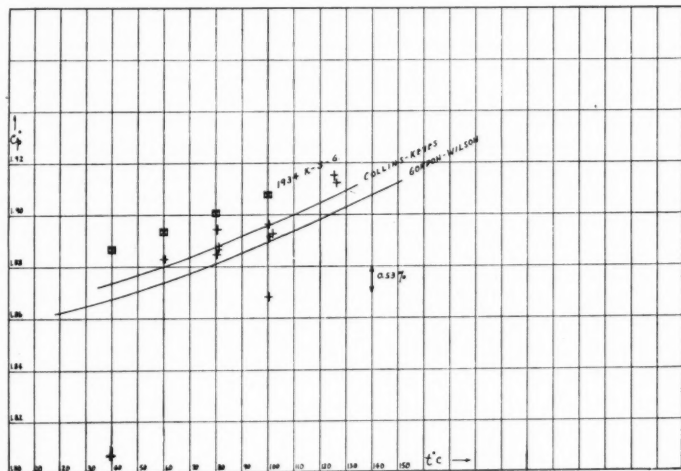


FIG. 3. Plot of Experimental Data for the Specific Heat of Steam with Computed Values.

computed values. The "Collins-Keyes" line is drawn from the empirical equation:

$$C_p^\circ = 1.47825 + 7.745 \cdot 10T^{-4} + \frac{47.8365}{T} \quad (7)$$

wherein the coefficients of T and T^{-1} are the same, as used to represent the G-W values. The "C-K" line is about one in three hundred above the G-W line for C_p° versus temperature.

The value of C_p° from the single measurement at $t_f 39.41^\circ \text{C}$ is

¹⁶ The curve is drawn from the equation representing the Gordon values of C_p° which is Eq. 22 of paper No. IV, obtained by Professor J. H. Keenan to which the E. Bright Wilson, Jr. term $4.08 \cdot 10^{-3} RT$ has been added.

3.3 percent low relative to the smoothed value. The measurement was made at an initial pressure of 50.26 mm. with a final pressure of 8.78 mm.; the pressure difference amounting to 41.48 mm. The control apparatus allowed a steady state to within about ± 0.01 mm. but small variations in pressure are more disturbing at lower pressures.¹⁷ Moreover the velocity effects already referred to are more pronounced at the lower pressures. It is regrettable that more measurements are not available at the lower temperatures but in the absence of apparatus improvements indicated in the course of the present work, additional measurements would not have been profitable.

The role of C_p° in the formulation of the equation for the enthalpy, H , is fundamental and in the equation 15A for steam¹⁸ the A. R. Gordon values were used. Allowance for the rotational distortion of the water molecule, made by E. Bright Wilson, Jr., increased the A. R. Gordon values by $4.08 \cdot 10^{-5}RT$ while the new experimental data suggests still larger values to the extent of a part in three hundred. This is an amount of the same order as the precision of the present measurements of C_p° which may accordingly be regarded as furnishing direct experimental evidence of the validity of Wilson's calculation, were confirmation necessary. Accepting the G-W values for C_p° , the steam enthalpy equation 15A of paper IV must be corrected by the addition of the term $9.4 \cdot 10^{-6} (T^2 - 273.16^2)$.¹⁹ Some of the con-

¹⁷A sudden change in pressure in the course of a measurement causes a temperature disturbance given approximately by the relation $\Delta T = -[RT/C_p p]\Delta p$, which indicates that ΔT will be large as the pressure is small.

¹⁸ Proc. Am. Acad. Arts and Sci. 70, 344 (1936)—Paper No. IV.

¹⁹ The new values of ψ_0 would only affect the values of H below 100° to a slight extent, but account must be taken of the fact that the present experiments give no reliable measure of ψ_1 . The equation of state extrapolated value of ψ_1^{100} is 0.979 I. j. while ψ_3 is 0.003, an entirely negligible quantity in the present state of our knowledge of steam properties. The following statement suggests a way of determining ψ_1 :

The measured value of the heat of evaporation (2256.6 I. j.) is probably known to a part in five thousand through the measurements of Osborne, Stimson, Fioch, and Ginnings working at the National Bureau of Standards. By using the Clapeyron equation and the known highly exact values of dp/dT along with the liquid volume at 100°, we may arrive at a quite precise value of the 100° saturation specific volume of steam, namely 1673.34 (equation of state gives 1673.3). Comparing this with the ideal-gas value for the volume at 100° and at atmosphere pressure, we obtain the gas defect amounting to $B = -26.61$ cc. which may be represented by $B = B^\circ + \varphi_1 p$. The value of B° and φ_1 from the equation of state are -25.07 and 1.593 respectively. The B° deduced from the present investigation is however -24.51 cc./g. so that

sequences arising from a comparison of these modified enthalpy values with existing experimental data are of interest.

There already exists a large body of measurements of the enthalpy, specific heat, and Joule-Thomson numbers for steam over wide ranges of pressure and of temperature, and further enthalpy data obtained by our colleagues in the program of steam investigation will be forthcoming in the near future. Further intercomparison of the data is therefore not profitable at this time. The comparisons that have been made, however, indicate that the values of enthalpy computed on the basis of the Gordon C_p° values and the equation of state are in very good agreement with, (a) the saturation enthalpy measurements of Osborne, Stimson, Fioch, and Ginnings, excluding computed values at saturation above about 340° where the equation of state is invalid; (b) the enthalpies from Havlicek and Miskovsky's²⁰ measurements over the superheat region to 550° to about a part in five hundred (the computed values, however, tend to be larger); (c) the latent heat measurements of Henning, Jakob, Jakob and Fritz; (d) the Knoblauch and Koch, and recent Koch heat capacity measurements, particularly the latter's recent measurements; and (e) the Harvard Joule-Thomson values by Davis and Kleinschmidt.

By way of summary it may be stated that while the measurements here presented confirm the Gordon-Wilson C_p° values and provide more reliable ψ_0 values, it is believed premature to reformulate the enthalpy equation in view of the excellent agreement with the published measurements. At a later time a comprehensive reduction of all available data using the G-W C_p° values²¹ may disclose a consistent trend indicating whether or not the equation of state is a sufficiently precise representation of the volume data.

we are led to the value -2.1 for φ_1 at 100° . In a reformulation of the equation of state in its present form, it would be necessary to make the φ_1 equation pass through this value along with similarly derived values from latent heats below 100° . We will not attempt this formulation at the moment since modern values for the latent heat are not yet available below 50° .

²⁰ *Helv. Phys. Acta*, *9*, 161 (1936).

²¹ In the August number of the *Physical Review* (1937) infra-red data for steam (rotation-vibration bands to $J = 11$) are reported by H. M. Randall, D. M. Dennison, Nathan Ginsburg, and Louis R. Weber. Further information on the moments of inertia of the molecule is also promised by the authors.

TABLE I
 EXPERIMENTAL DATA FOR LOW PRESSURE STEAM

t_i °C.	P_i Atm.	P_f Atm.	$(P_i - P_f)$ Atm.	$(T_f - T_i)$	$(H_f - H_i)$ Joules/gram	Rate of flow Gram/sec.
38.94	0.06404	0.00786	0.05618	0.0142	1.68977	0.001255
	0.06613	0.01155	0.05458	0.9484	3.33999	0.001291
59.44	0.17736	0.00784	0.16952	0.0021	3.65592	0.005495
	0.17898	0.01228	0.16670	0.9668	5.42030	0.005311
	0.18040	0.01251	0.16789	1.6850	6.80378	0.005409
80.02	0.18087	0.01246	0.16842	0.0028	2.63888	0.005110
	0.18272	0.01260	0.17012	1.5554	5.61078	0.005189
	0.30942	0.01926	0.29016	0.0100	4.64590	0.010514
	0.31016	0.01926	0.29090	1.1224	6.75823	0.010548
	0.31088	0.01843	0.29245	2.0280	8.49656	0.010567
	0.31042	0.01774	0.29268	2.0014	8.45166	0.010611
100.00	0.18125	0.01148	0.16977	0.0051	2.05506	0.004819
	0.18173	0.01227	0.16945	1.1899	4.29753	0.004824
	0.26455	0.01567	0.24888	0.0291	3.06378	0.008103
	0.26564	0.01614	0.24950	1.7408	6.31702	0.008120
	0.26494	0.01574	0.24920	4.1370	10.85447	0.008057
	0.48150	0.02731	0.45418	0.0763	5.72909	0.017621
	0.48672	0.02689	0.45983	1.7271	8.92784	0.017802
125.00	0.18988	0.01153	0.17835	0.0033	1.61055	0.004781
	0.18963	0.01145	0.17818	1.6436	4.75247	0.004752
	0.19451	0.01157	0.18294	3.2307	7.82712	0.004911
	0.29198	0.01613	0.27585	0.0218	2.45406	0.008654
	0.29583	0.01731	0.27852	0.0496	2.60916	0.008689

TABLE II

ENTHALPY COEFFICIENTS

	Smoothed $-\psi_{0**}$	Obs. $-\psi_0$ I.j.	Eq.St. $-\psi_0$ I.j.	Obs. $-\psi_1$ I.j.	Eq.St. $-\psi_1$ I.j.
38.94	29.08	28.859*	33.581		10.395
59.44	20.48	20.774*	23.050		4.150
80.02	15.266	15.195	16.616	2.283	1.910
100.00	11.852	11.871	12.574	0.832	0.979
125.00	8.931	8.916	9.269	0.395	0.461

* Deduced from experimental data using ψ_1 from equation of state. Equation for $\psi_1 = [-0.9906\tau^7 \cdot 10^{18} + 1.318\tau^{14} \cdot 10^{26} - 1.1732\tau^{21} \cdot 10^{34}]$ I.j.

** $\Delta\psi_0 = \psi_0^{\text{obs.}} - \psi_0^{\text{eq. st.}} = [5.45\tau^{12} \cdot 10^{30} - 1.373\tau^{24} \cdot 10^{60}]$ I.j.

TABLE III

COMPUTED VALUES OF C_p° FOR STEAM: I.J. PER GRAM

T_i	
38.94	1.8068 (39.41)
59.44	1.8828 (59.92) : 1.8827 (60.28)
80.02	1.8845 (80.58) : 1.8943 (80.80) : 1.8879 (81.02) : 1.8865 (81.03)
100.00	1.8963 (100.59) : 1.8915 (100.87) : 1.8924 (102.07) : 1.8681 (100.86)
125.00	1.9151 (125.82) : 1.9121 (126.62)

The numbers in brackets represent the average temperature.

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2. *Handwritten text, possibly a subtitle or second header.*

3. *Handwritten text, possibly a date or reference.*

